1. Introduction

Increased dephosphorization in steelmaking processes and the use of high phosphorus content iron ore in recent years has resulted in higher phosphorus content in the slag, which, if recycled to iron- and steel-making processes, leads to phosphorus enrichment in hot metal, hence the reuse of the slag is limited. Alternatively, if slag is used directly as a raw material for phosphoric fertilizer it is too low in P for effective use. Therefore, if P\textsubscript{2}O\textsubscript{5} in the slag can be enriched and separated, the separated P\textsubscript{2}O\textsubscript{5} phase may be used as phosphoric fertilizer additives, and the remainder may be recycled to iron- and steel-making processes, such as sintering, hot metal desiliconization, and hot metal dephosphorization process, so the utilization of converter slag in agriculture area is promoted, the environmental pollution is solved and economic benefits is created.

Using of slag phosphate fertilizer has hundreds years of history, in the country with rich phosphorus containing iron ore such as France, Germany etc., slag phosphate fertilizer always has big share, accounts for 13–16% of total phosphate fertilizer. However, blast furnace slag and steel slag used as agricultural fertilizer and soil improvement is totally 230 000 tons in China 2010, accounts for 0.5% of total blast furnace slag and steel slag using amount, so the utilization of steel slag for fertilizer is very low.

It is well known that fluor spar is a commonly used additive to lower the melting point and viscosity of slag in steelmaking processes, and then promote dephosphorization process, but CaF\textsubscript{2} in slag can seriously corrode of refractory and pollute the environment. Slag phosphate fertilizer can not be dissolved in water, but can be dissolved in 2% citric acid solution. So the slag phosphate fertilizer belongs to citrate-soluble phosphatic fertilizer, and its fertilizer efficiency is determined by P\textsubscript{2}O\textsubscript{5} content and P\textsubscript{2}O\textsubscript{5} solubility. The CaF\textsubscript{2} in the slag can easily react with Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} to produce fluorapatite phase (Ca\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}F), which has the significant influence on P\textsubscript{2}O\textsubscript{5} solubility. Therefore, considering the environmental problem and the high-phosphorus slag can be used as slag phosphate fertilizer, the use of a small amount of Na\textsubscript{2}O instead of CaF\textsubscript{2} can play a role to help melt...
slag in slagging process. Some scholars have made a lot of research on the slag phosphorus existence form \(^6{-11}\) and magnetic separation behavior,\(^{12-16}\) K. Yokoyama \textit{et al.}\(^{17}\) found that phosphorus existed mainly in the form of nC\(_2\)S–C\(_3\)P solid solution in the slag, and firstly proposed phosphorus recover from the steelmaking slag by magnetic separation. But the systematic research on the effect of Na\(_2\)O on resource utilization of P-bearing slag is less. In view of this, this paper researches systematically the influence of Na\(_2\)O in P-bearing slag on phosphorus existence form, P\(_2\)O\(_5\) solubility and magnetic separation behavior, which provide the necessary research basis for the utilizing of P-bearing slag.

2. Research Method

2.1. P-bearing Slag Thermal Experimental
Reagent-grade CaO, SiO\(_2\), Fe\(_2\)O\(_3\), P\(_2\)O\(_5\) and Na\(_2\)CO\(_3\) were used to produce slag in this experiment. Then, the reagents were mixed in various ratios in order to produce the CaO–SiO\(_2\)–Fe\(_2\)O\(_3\)–P\(_2\)O\(_5\) slag system. For investigating the effect of Na\(_2\)O on phosphorus enrichment and separation, Na\(_2\)O were added in some cases. The mixing conditions are summarized in Table 1. Figure 1 also shows the composition range of the used slag on the CaO–SiO\(_2\)–Fe\(_2\)O\(_3\) phase diagram that calculated by FactSage 6.3 for samples X. As shown in Fig. 1, all experimental slag are in the dicalcium silicate (C\(_2\)S) primary zone, C\(_2\)S was precipitated firstly during the cooling process, and so nC\(_2\)S–C\(_3\)P solid solution (mainly Ca\(_{15}\)(PO\(_4\))\(_2\)(SiO\(_4\))\(_6\) and Ca\(_5\)(PO\(_4\))\(_2\)SiO\(_4\)) was easily formed. Adding Na\(_2\)O into slag can be used as a flux to instead of fluorite for slag forming in dephosphorization process, and most of the iron oxide would be in the form of FeO in steelmaking condition, but Fe\(_2\)O\(_3\) was used as iron oxide in this experiment, the reasons are as follow: 1) Ito \textit{et al.}\(^{18}\) has shown that the distribution behavior of P\(_2\)O\(_5\) between solid solution and liquid phases was not different, when the iron oxide was changed from FeO to Fe\(_2\)O\(_3\). 2) Shimauchi \textit{et al.}\(^{14}\) found that FeO was solved into the solid solution but the content of Fe\(_2\)O\(_3\) in solid solution was negligible small. 3) By the preliminary experiments, it was found that phosphorus enrichment behavior between solid solution and liquid phases was no affected, when the iron oxide was changed from FeO to Fe\(_2\)O\(_3\).

The mixed slag (200 g) was placed in a magnesia crucible 60 mm dia×100 mm, placed inside a graphite crucible and heated in a MoSi\(_2\) electric resistance furnace up to 1 773 K, and maintained the temperature for 30 minutes to ensure slag fully melting. Then the slag was cooled to 1 623 K at a cooling rate of 3 K/min, kept at this temperature for 1 hour in order to fully promote the precipitation of 3CaO·P\(_2\)O\(_5\), then cooled to 1 423 K at a cooling rate of 3 K/min, the furnace was then closed and the slag sample was cooled within it (see Fig. 2), and the heat treatment was performed in an air atmosphere. After each experiment the slag was ground (less than 300 mesh (48 \(\mu\)m)), mineralogical phases were determined by XRD analysis. Diffraction patterns were measured in a 2\(^\text{θ}\) range of 10–90\(^\text{°}\) using copper K\(_{\alpha}\) radiation of 40 kV and 30 mA, and the scan speed was 5\(^\text{°}\)/min.

2.2. P\(_2\)O\(_5\) Solubility Experimental of P-bearing Slag
The quinoline phosphomolybdate gravimetric method provided by national standard GB20412-2006 is used to measure the P\(_2\)O\(_5\) solubility of P-bearing slag. 1.0000 g P-bearing slag ground to less than 300 meshes (48 \(\mu\)m) has been prepared, and then it was put in a dry 250 mL volumetric flask. Accurately added 150 mL, 301–303 K 2% citric acid solution into the volumetric flask, kept the temperature in the range of 301–303 K, and put the volumetric flask on oscillator to shake for one hour. After adding water in volumetric flask to the tick mark, the solution was blended and filtered. Certain sample solution was poured into a 500 mL beaker, and 10 mL 1:1 nitric acid solution was added, then water was added into the beaker to dilute to 100 mL. Sample solution was heated to boil. Then 35 mL quimociac was added into the beaker, and reacted with the
$\text{P}_2\text{O}_5$ in sample solution and precipitated as yellow quinoline phosphomolybdate. And then the beaker was covered with watch glass, heated it again to micro-boil to make the sediment layered, and the beaker was taken out to cool to ambient temperature. The glass filter which has been put in a 453 K drying oven to dry to constant weight was used to filter, then put the precipitation and glass filter in the 453 K drying oven to dry for 45 min. At last, the precipitation and glass filter were taken out to cool and weight. Meanwhile, the blank experimental is also done. The main reaction in experiment is Eq. (1). Figure 3(a) is the picture of extracted quinoline phosphomolybdate precipitation, Fig. 3(b) is the blank experiment for comparison.

$$\text{H}_3\text{PO}_4 + 12\text{MoO}_2^2+ + 24\text{H}^+ + 3\text{Ca}_3\text{H}_2\text{N} = (\text{C}_3\text{H}_2\text{N})_3\text{H}_3(\text{PO}_4, 12\text{MoO}_2)^- + 12\text{H}_2\text{O} \quad \text{...... (1)}$$

The effective $\text{P}_2\text{O}_5$ content dissolved in 2% citric acid solution was calculated, and then the slag $\text{P}_2\text{O}_5$ solubility expression is shown in Eq. (2), where $\left(\%\text{P}_2\text{O}_5\right)_{\text{Available}}$, $\left(\%\text{P}_2\text{O}_5\right)_{\text{Total}}$ is the $\text{P}_2\text{O}_5$ content that can be dissolved in 2% citric acid solution and total $\text{P}_2\text{O}_5$ content in slag respectively, (P$_2$O$_5$)$_{\text{Solubility}}$ is slag $\text{P}_2\text{O}_5$ solubility.

$$\left(\text{P}_2\text{O}_5\right)_{\text{Solubility}} = \frac{\left(\%\text{P}_2\text{O}_5\right)_{\text{Available}}}{\left(\%\text{P}_2\text{O}_5\right)_{\text{Total}}} \quad \text{...... (2)}$$

### 2.3 Magnetic Separation Experimental of P-bearing Slag

Magnetic separation experiments of the P-bearing slag were done with a DTCXG-ZN50 magnetic separator tube of 50 mm diameter. The swing frequency was 70 times per minute, travelling stroke was 40 mm and the air gap between the magnetic poles was 52 mm. The magnetic separator tube is schematically illustrated in Fig. 4. A 10 g slag sample was put into the solution mixed with alcohol and water. The magnetic field intensity of the separator tube was adjusted to a predetermined intensity, electric motor was actuated to make the tube vibrated. Sample solution was poured into the magnetic separator tube and vibrated with the tube, then magnetic substances attached to the tube wall, and non-magnetic substances flowed into the prepared container outside the tube with the aid of mechanical vibration. The magnetic and non-magnetic substances were dried at 378 K for 12 hours, weighed and analyzed.

### 3. Experiment Results and Discussion

#### 3.1 The Effect of Na$_2$O on Phosphorus Existence Form in P-bearing Slag

##### 3.1.1 The Effect of Na$_2$O on Melting Point of P-bearing Slag

The melting points of the synthetic slag are calculated by FactSage6.3, the results are shown in Table 2. It can be seen from the results, the melting point of the A, B and C slag are 1 583 K, 1 469 K and 1 283 K respectively. And with the increasing of Na$_2$O content in slag, the melting point of slag is obviously increased. The results show that Na$_2$O has good fluxing action for the steelmaking slag, and can be used as a flux to instead of fluorite for slag forming in steelmaking process.

##### 3.1.2 Thermodynamic Analysis of Effect of Na$_2$O on Phosphorus Existence Form in P-bearing Slag

During slag cooling process, Ca, Si, P and O in the slag were precipitated firstly in the form of $6\text{C}_2\text{S}–\text{C}_3\text{P}$ solid solution. The generation reaction of early precipitated low phosphorus solid solution ($6\text{C}_2\text{S}–\text{C}_3\text{P}$) reacts with Na$_2$O in slag to produce high phosphorus solid solution ($\text{Na}_2\text{Ca}_2(\text{PO}_4)_2\text{Si}_2\text{O}_7$). The generation reaction of P-bearing solid solution in P-bearing slag is as follows:

$$12\text{CaO} + 6\text{SiO}_2 + \text{Ca}_3(\text{PO}_4)_2 = 6\text{Ca}_2\text{SiO}_4 \cdot \text{Ca}_3(\text{PO}_4)_2$$

$$\Delta G_1 = \Delta G_1^0 + RT \ln \frac{a_{\text{Ca}_2\text{SiO}_4} \cdot a_{\text{Ca}_3(\text{PO}_4)_2}}{a_{\text{CaO}} \cdot a_{\text{SiO}_2} \cdot a_{\text{Ca}_3(\text{PO}_4)_2}} \quad \text{...... (3)}$$

$$\text{Na}_2\text{O} + 6\text{Ca}_2\text{SiO}_4 \cdot \text{Ca}_3(\text{PO}_4)_2 = \text{Na}_2\text{Ca}_2(\text{PO}_4)_2 \cdot 5\text{Ca}_2\text{SiO}_4 + \text{CaO}$$

$$\Delta G_2 = \Delta G_2^0 + RT \ln \frac{\text{Ca}_2\text{SiO}_4 \cdot \text{Ca}_3(\text{PO}_4)_2 \cdot a_{\text{Na}_2\text{O}}}{a_{\text{SiO}_2} \cdot a_{\text{Na}_2\text{Ca}_2(\text{PO}_4)_2}} \quad \text{...... (4)}$$

Where $a_{\text{SiO}_2}$, $a_{\text{CaO}}$, $a_{\text{Na}_2\text{O}}$, $a_{\text{Ca}_2\text{SiO}_4}$, $a_{\text{Ca}_3(\text{PO}_4)_2}$, $a_{\text{Na}_2\text{Ca}_2(\text{PO}_4)_2}$, $a_{\text{Na}_2\text{Ca}_2(\text{PO}_4)_2}$, $a_{\text{SiO}_2}$, and $a_{\text{Na}_2\text{Ca}_2(\text{PO}_4)_2}$ are respectively the activity of $\text{SiO}_2$, $\text{CaO}$, $\text{Na}_2\text{O}$, $\text{Ca}_2\text{SiO}_4$, $\text{Ca}_3(\text{PO}_4)_2$, $\text{Na}_2\text{Ca}_2(\text{PO}_4)_2$, $\text{SiO}_2$, and $\text{Na}_2\text{Ca}_2(\text{PO}_4)_2$. $\Delta G_1$ and $\Delta G_2$ respectively shows the Gibbs free energy of reaction (3) and (5);

<table>
<thead>
<tr>
<th>No.</th>
<th>Melting point / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1 583</td>
</tr>
<tr>
<td>B</td>
<td>1 469</td>
</tr>
<tr>
<td>C</td>
<td>1 283</td>
</tr>
</tbody>
</table>
shows that the generation amount of 
\( \text{Na}_2\text{O} \) content
and the increasing of Na\(_2\text{O}\) content
is less than 3% when Na\(_2\text{O}\) content
in the reaction (3)
can also be considered the effect on
\( \{\text{CaCO}_3 \} \).}

During slag cooling process, large amount Ca\(_2\text{SiO}_4\)
is precipitated and reacted with Ca\(_3(\text{PO}_4)_2\) to generate 6C\(_2\text{S}–\text{C}_3\text{P}\) solid solution. **Figure 5** is the curve of the logarithm part oxides activity change with Na\(_2\text{O}\) content at 1 623 K that calculated by FactSage6.3, and the FactPS and FT Oxid database was used in the calculation process. **Figure 5** shows that the value of \( \{\text{Ca}_2\text{SiO}_4 \} \)
and thermodynamic trend of Ca\(_2\text{SiO}_4\) phase generation. But the decreasing of \( \{\text{Ca}_2\text{SiO}_4 \} \)
shows that the generation amount of 6C\(_2\text{SiO}_4\) phase is reduced slightly.

With the increasing of Na\(_2\text{O}\) content in slag, \( \{\text{Ca}_2\text{SiO}_4 \}, \{\text{aCaO}, \{\text{Ca}_2\text{SiO}_4 \} \}
and \( \{\text{aCaO}, \{\text{Ca}_2\text{SiO}_4 \} \}\)
are decreased. The decreasing of \( \{\text{aCaO}, \{\text{Ca}_2\text{SiO}_4 \} \}\)
is less than 3% when Na\(_2\text{O}\) content from 1% to 5%, and has little effect on Gibbs free energy of reaction (3), which also shows that the increasing of Na\(_2\text{O}\) content has little effect on early precipitation of 6C\(_2\text{S}–\text{C}_3\text{P}\) solid solution, so the precipitation amount of 6C\(_2\text{S}–\text{C}_3\text{P}\) solid solution is reduced gradually. Meanwhile, the increasing of \( \{\text{Ca}_2\text{SiO}_4 \} \)
and the decreasing of \( \{\text{Ca}_2\text{SiO}_4 \} \)
can also reflect the occurrence of the reaction (5) and (7).

When the Na\(_2\text{O}\) content exceeds a certain level, the P-bearing solid solution (6C\(_2\text{S}–\text{C}_3\text{P}\)) and Na\(_2\text{Ca}_4(\text{PO}_4)_2\text{SiO}_4\) generated by above mentioned reaction continue to react with Na\(_2\text{O}\), then high phosphorus solid solution Na\(_3\text{PO}_4\) is generated, the early precipitated solid solution is dissolved.

\[3\text{Na}_2\text{O}+2\text{Na}_2\text{Ca}_4(\text{PO}_4)_2\text{SiO}_4=2\text{Na}_3\text{PO}_4+2\text{Ca}_2\text{SiO}_4+2\text{C}_3\text{P} \]

\[\Delta G_7=\Delta G_7^0+RT\ln\frac{a_{\text{Ca}_3(\text{PO}_4)_2(\text{SiO}_4)}}{a_{\text{Na}_2\text{Ca}_4(\text{PO}_4)_2\text{SiO}_4}} \]

Where \( \{\text{Ca}_3(\text{PO}_4)_2 \}, \{\text{Na}_2\text{Ca}_4(\text{PO}_4)_2\text{SiO}_4 \}, \{\text{Na}_3\text{PO}_4 \}, \{\text{Na}_2\text{Ca}_4(\text{PO}_4)_2\text{SiO}_4 \}
and \( \{\text{Na}_3\text{PO}_4 \} \)
is respectively the activity of Ca\(_3\text{PO}_4\), Na\(_2\text{Ca}_4(\text{PO}_4)_2\text{SiO}_4\), Na\(_3\text{PO}_4\), Na\(_2\text{Ca}_4(\text{PO}_4)_2\text{SiO}_4\)
and 6Ca\(_2\text{SiO}_4\) Ca\(_3(\text{PO}_4)_2\text{SiO}_4\). \( \Delta G_7 \) shows the Gibbs free energy of reaction (7), 6Ca\(_2\text{SiO}_4\) Ca\(_3(\text{PO}_4)_2\text{SiO}_4\) can be regarded as pure substances, and their activity is 1.

Similarly, the thermodynamic trend of reaction (7) and the generation amount of Na\(_3\text{PO}_4\) is determined by \( \{\text{Ca}_2\text{SiO}_4 \}, \{\text{aCaO}, \{\text{Ca}_2\text{SiO}_4 \} \}\)
and phosphorus enrichment of this phase is also effected by \( \{\text{Ca}_2\text{SiO}_4 \}, \{\text{aCaO}, \{\text{Ca}_2\text{SiO}_4 \} \} \).

With the increasing of Na\(_2\text{O}\) content, Ca and Si content in P-rich phase is decreased and P content is increased, EDS detection results also shows that in **Table 3**.

According to the above mentioned description, when the Na\(_2\text{O}\) content is less than 6% in slag, Na\(_2\text{O}\) content in slag has little effect on the early precipitation of P-bearing solid solution (6C\(_2\text{S}–\text{C}_3\text{P}\)) during the cooling process, when the Na\(_2\text{O}\) content is more than 6%, with the increasing of Na\(_2\text{O}\) content, early precipitation trend of P-bearing solid solution (6C\(_2\text{S}–\text{C}_3\text{P}\)) is reduced. When the temperature is dropped to about 1 623 K, the early precipitated low phosphorus solid solution (6C\(_2\text{S}–\text{C}_3\text{P}\)) reacts with Na\(_2\text{O}\) in slag to
produce high phosphorus solid solution (Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$) or (C$_2$S–C$_3$P), and until the low phosphorus solid solution (6C$_2$S–C$_3$P) is disappeared. When the Na$_2$O content is continuously increased until excess, proportion of Ca and Si is reduced in the high phosphorus solid solution (Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$) that generated by the above mentioned reaction, then more high phosphorus solid solution (Na$_3$PO$_4$) are generated, so the phosphorus content in the phosphorus-rich phase is increased accordingly.

### 3.1.3. The Effect of Na$_2$O on Phosphorus Existence Form in P-bearing Slag

Figure 6 is SEM-BSE image corresponding to the Table 3 sample with furnace cooling. Table 3 is the EDS results corresponding to figure 6 sample compositions. Figure 7 is the XRD results of A and C slag.

| No. | Main phase | Na$_2$O | MgO | SiO$_2$ | P$_2$O$_5$ | CaO | Fe$_2$O$_3$
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>A</td>
<td>P-rich phase</td>
<td>0</td>
<td>2.95</td>
<td>15.24</td>
<td>20.75</td>
<td>58.90</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>RO phase</td>
<td>0</td>
<td>5.30</td>
<td>0.07</td>
<td>0.17</td>
<td>0.61</td>
<td>93.85</td>
</tr>
<tr>
<td></td>
<td>Base phase</td>
<td>0</td>
<td>11.46</td>
<td>31.29</td>
<td>3.56</td>
<td>53.68</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>P-rich phase</td>
<td>2.16</td>
<td>0</td>
<td>14.58</td>
<td>23.63</td>
<td>59.61</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>RO phase</td>
<td>0</td>
<td>7.82</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>92.18</td>
</tr>
<tr>
<td></td>
<td>Base phase</td>
<td>1.47</td>
<td>9.54</td>
<td>23.13</td>
<td>2.23</td>
<td>63.60</td>
<td>1.03</td>
</tr>
<tr>
<td>C</td>
<td>P-rich phase</td>
<td>12.31</td>
<td>0</td>
<td>8.63</td>
<td>31.74</td>
<td>47.01</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>RO phase</td>
<td>0.85</td>
<td>8.03</td>
<td>0.35</td>
<td>0.15</td>
<td>0</td>
<td>90.62</td>
</tr>
<tr>
<td></td>
<td>Base phase</td>
<td>3.70</td>
<td>10.52</td>
<td>22.51</td>
<td>1.45</td>
<td>60.30</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Fig. 6. SEM-BSE image of experimental samples A, B, C (1- P-rich phase, 2- RO phase, 3- Base phase).

Fig. 7. X-ray diffraction patterns of A slag and C slag.

It can be seen from the results, the A, B and C slag mainly contains phosphorus-rich phase, base phase and RO phase. It can be seen from the results, the A, B and C slag mainly contains phosphorus-rich phase, base phase and RO phase. The phosphorus content in base phase is low, and base phase mainly consists of nCaO·SiO$_2$, and the RO phase mainly consists of iron oxide or iron and magnesium oxide.

P$_2$O$_5$ content of the phosphorus-rich phase in A slag is about 20%, the phosphorus in phosphorus-rich phase is mainly in the existence of Ca$_{15}$(PO$_4$)$_2$(SiO$_4$)$_6$ solid solution. After the addition of 3% Na$_2$O, P$_2$O$_5$ content of the phosphorus-rich phase in B slag is increased obviously compared with A slag, the added Na$_2$O mainly replaces calcium ions(Ca$^{2+}$) in phosphorus-rich phase (Ca$_{15}$(PO$_4$)$_2$(SiO$_4$)$_6$ solid solution) to form the Ca$_5$(PO$_4$)$_2$SiO$_4$ and Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$, finally the phosphorus-rich phase is mainly Ca$_{15}$(PO$_4$)$_2$(SiO$_4$)$_6$, Ca$_5$(PO$_4$)$_2$SiO$_4$ exists along with Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$, and P$_2$O$_5$ content of the phosphorus-rich phase is generally about 23–26%, and the particle size is further increased. For the C slag, P$_2$O$_5$ content of the phosphorus-rich phase is further increased to 32%, and owning to the binding capacity of sodium ions(Na$^+$) combine with phosphate ions are stronger than calcium ions(Ca$^{2+}$), calcium ions(Ca$^{2+}$) in phosphorus-rich phase (6C$_2$S–C$_3$P or Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$) are replaced by sodium ions(Na$^+$), then Na$_3$PO$_4$ is formed, so the phosphorus existence form is changed.

### 3.2. The Effect of Na$_2$O on P$_2$O$_5$ Solubility of P-bearing Slag

It can be seen from Table 3, with the addition of Na$_2$O, P$_2$O$_5$ content in solid solution is relatively increased which is beneficial to phosphorus enrichment in solid solution. And adding Na$_2$O into CaO–SiO$_2$–P$_2$O$_5$–Fe$_2$O$_3$ slag system can break the complex net structure formed by Si-O on certain degree, and also can hinder the precipitation of Ca$_3$(PO$_4$)$_2$ crystal with low P$_2$O$_5$ solubility during the melting-cooling process. Therefore adding appropriate Na$_2$O content into CaO–SiO$_2$–P$_2$O$_5$–Fe$_2$O$_3$ slag system can improve the slag P$_2$O$_5$ solubility, as shown in Fig. 8. For B(3%Na$_2$O) and C(6%Na$_2$O) slag, owing to adding Na$_2$O into slag, calcium ions(Ca$^{2+}$) in phosphorus-rich phase (6C$_2$S–C$_3$P solid solution) are partly replaced by sodium ions(Na$^+$), then Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$ and Na$_3$PO$_4$ are formed, so the phosphorus existence form is changed. But these compounds (Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$ and Na$_3$PO$_4$) and phosphorus-rich phase (6C$_2$S–C$_3$P solid solution) have almost same good citric acid solubility, so P$_2$O$_5$ solubility of the B slag and C slag have little difference. Therefore, adding appropriate Na$_2$O content into slag can improve the slag P$_2$O$_5$ solubility, but the effect of different amounts of Na$_2$O on the P$_2$O$_5$ solubility has little difference.

### 3.3. The Effect of Na$_2$O on Magnetic Separation of P-bearing Slag

The magnetic separation experiment of the A and C slag was carried out under magnetic field intensity of 350 mT
and particle size of 300 meshes (48 μm). The experimental method is shown in Sec. 2.3. The phosphorus-rich phase is diamagnetism and enters into non-magnetic substances after magnetic separation. The following expressions describe the phosphorus and iron distribution in magnetic substances and non-magnetic substances.

\[ L_P = \frac{\text{%P}_2\text{O}_5 \cdot M_1}{\text{%P}_2\text{O}_5 \cdot M_2} \quad \text{(9)} \]

\[ H_{P,i} = \frac{\text{%P}_2\text{O}_5 \cdot M_i}{\text{%P}_2\text{O}_5 \cdot M_2 + \text{%P}_2\text{O}_5 \cdot M_1} \quad \text{(i = 1 or 2)} \quad \text{(10)} \]

\[ H_{\text{Fe},i} = \frac{\text{%TFe} \cdot M_i}{\text{%TFe} \cdot M_2 + \text{%TFe} \cdot M_1} \quad \text{(i = 1 or 2)} \quad \text{(11)} \]

Where M_1, M_2 is respectively non-magnetic and magnetic substances mass, (g); (%P_2O_5)_1, (%P_2O_5)_2 is respectively P_2O_5 mass fraction of non-magnetic and magnetic substances, (%); L_P is the phosphorus distribution ratio between non-magnetic and magnetic substances; (%TFe)_i, (%TFe)_2 is respectively TFe mass fraction of non-magnetic and magnetic substances, (%); H_P is the P_2O_5 percentage from slag enters into non-magnetic or magnetic substances; H_{\text{Fe},i} is the TFe percentage from slag enters into non-magnetic or magnetic substances; the phosphorus recovery rate and iron recovery rate is respectively P_2O_5 percentage enters into non-magnetic substances and TFe percentage enters into magnetic substances.

The proportion of magnetic substances and non-magnetic substances in A slag and C slag is shown in Fig. 9. As shown in Fig. 9, the phosphorus recovery rate in non-magnetic substances is 64.55% in A slag after magnetic separation. While the phosphorus recovery rate in non-magnetic substances is 36.53% in C slag after adding 6% Na_2O. Na_2O can obviously improve the phosphorus enrichment effect in phosphorus-rich phase of P-bearing slag, and the P_2O_5 content is high in non-magnetic substances after magnetic separation. But Na_2O also can improve the metallization of slag and magnetism of iron-rich phase, make the magnetic substances content increased and separation of phosphorus and iron is incomplete, thus the phosphorus recovery rate is decreased instead. Therefore, Na_2O content in slag has an important influence on the slag magnetic separation, and the Na_2O content in slag must be controlled to obtain higher phosphorus recovery rate.

4. Conclusions

The phosphorus resources recovery and utilization of P-bearing steelmaking slag were fully researched, and the effect of Na_2O instead of CaF_2 in slagging process on resource utilization of P-bearing slag used as slag phosphate fertilizer was analyzed. The key findings are as follows:

(1) The slag contains phosphorus-rich phase, base phase and RO phase. The phosphorus in slag is mainly in the form of nC_2S–C_3P solid solution in the phosphorus-rich phase. The melting point of slag decreases obviously and the phosphorus content in the phosphorus-rich phase increases obviously after adding suitable Na_2O into slag. P_2O_5 content is about 30%, which can fully meet the requirement of phosphorus content of phosphatic fertilizer.

(2) The P-bearing steelmaking slag after adding Na_2O firstly precipitate P-bearing solid solution phase (6C_2S–C_3P) during the cooling process. When the temperature is dropped to about 1 623 K, early precipitated low phosphorus solid solution (6C_2S–C_3P) react with Na_2O in slag to produce high phosphorus solid solution (Na_2Ca_4(PO_4)_2SiO_4), and until the low phosphorus solid solution (6C_2S–C_3P) is disappeared. When the Na_2O content is excessive, the high phosphorus solid solution(Na_2Ca_4(PO_4)_2SiO_4) that generated by the above mentioned reaction will continue to react with Na_2O to produce Na_2PO_4, then the P_2O_5 content in P-bearing solid solution is increased. So the suitable Na_2O content in slag is beneficial to the phosphorus enrichment in the phosphorus-rich phase.

(3) When adding Na_2O into CaO–SiO_2–Fe_2O_3–P_2O_5 slag system, the slag citric acid solubility is generally more than 90%. And adding Na_2O into CaO–SiO_2–P_2O_5–Fe_2O_3 slag system can break the complex net structure formed by Si–O on certain degree, and also hinders the precipitation of β-Ca_3(PO_4)_2 crystal with low citric acid solubility during the melting-cooling process, so adding appropriate Na_2O content in CaO–SiO_2–P_2O_5–Fe_2O_3 slag can improve the slag P_2O_5 solubility. While for CaO–SiO_2–P_2O_5–Fe_2O_3–Na_2O slag system, the effect of different amounts of Na_2O on the P_2O_5 solubility has little difference, which is mainly due to sodium ions(Na^+) in Na_2O can partly replaced calcium ions(Ca^+) in phosphorus-rich phase (6C_2S–C_3P solid solution), then Na_2Ca_4(PO_4)_2SiO_4 and Na_2PO_4 are formed, and they and phosphorus-rich phase (6C_2S–C_3P solid solution)
have almost same good citric acid solubility.

(4) Na$_2$O can obviously increase the phosphorus enrichment of phosphorus-rich phase in slag and P$_2$O$_5$ solubility, but Na$_2$O also can improve the metallization of slag and magnetism of iron-rich phase, make the magnetic substances content increased and separation of phosphorus and iron is incomplete, so it is adverse to phosphorus resources recovery. Therefore, adding appropriate Na$_2$O content (<6%) into slag can be used as a flux to instead of fluorite for slag forming in steelmaking process, while the phosphorus enrichment of phosphorus-rich phase in slag and P$_2$O$_5$ solubility is obviously increased, phosphorus resources recovery is assured to slightly decrease, it is beneficial to recycle the phosphorus in P-bearing converter slag.

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